

**PATENT APPLICATION**

**Attorney Docket No. D/99532**

**APPLICATION FOR  
UNITED STATES LETTERS PATENT**

**TO WHOM IT MAY CONCERN:**

Be it known that I, **Shadi L. Malhotra**, citizen of Canada and residing at 4191 Taffey Crescent, Mississauga, Ontario, L5L 2A6, have invented

**Hot Melt Inks Containing Styrene or Terpene Polymers**

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Date of Deposit: September 23, 1999

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*Charlene A. Szydlowski* Date: 9/23/99  
Charlene A. Szydlowski

04/20/99 "04/20/99"

**HOT MELT INKS CONTAINING STYRENE OR TERPENE POLYMERS**

**BACKGROUND OF THE INVENTION**

5 The present invention is directed to hot melt ink compositions. More specifically, the present invention is directed to ink compositions suitable for use in hot melt acoustic ink printing processes. One embodiment of the present invention is directed to an ink composition comprising (a) a styrene polymer or terpene polymer hardening component, (b) a nonpolymeric aromatic viscosity modifier,  
10 (c) a colorant, (d) an optional nonpolymeric aromatic ink vehicle, (e) an optional colorant dispersing agent, (f) an optional conductivity enhancing agent, (g) an optional antioxidant, and (h) an optional UV absorber.

Acoustic ink jet printing processes are known. In acoustic  
15 ink jet printing processes, an acoustic beam exerts a radiation pressure against objects upon which it impinges. Thus, when an acoustic beam impinges on a free surface (i.e., liquid/air interface) of a pool of liquid from beneath, the radiation pressure which it exerts against the surface of the pool may reach a sufficiently high level to release individual  
20 droplets of liquid from the pool, despite the restraining force of surface tension. Focusing the beam on or near the surface of the pool intensifies the radiation pressure it exerts for a given amount of input power. These principles have been applied to prior ink jet and acoustic printing proposals. For example, K. A. Krause, "Focusing Ink Jet Head,"

IBM Technical Disclosure Bulletin, Vol. 16, No. 4, September 1973, pp. 1168-1170, the disclosure of which is totally incorporated herein by reference, describes an ink jet in which an acoustic beam emanating from a concave surface and confined by a conical aperture was used to propel ink droplets out through a small ejection orifice. Acoustic ink printers typically comprise one or more acoustic radiators for illuminating the free surface of a pool of liquid ink with respective acoustic beams. Each of these beams usually is brought to focus at or near the surface of the reservoir (i.e., the liquid/air interface). Furthermore, printing conventionally is performed by independently modulating the excitation of the acoustic radiators in accordance with the input data samples for the image that is to be printed. This modulation enables the radiation pressure which each of the beams exerts against the free ink surface to make brief, controlled excursions to a sufficiently high pressure level for overcoming the restraining force of surface tension. That, in turn, causes individual droplets of ink to be ejected from the free ink surface on demand at an adequate velocity to cause them to deposit in an image configuration on a nearby recording medium. The acoustic beam may be intensity modulated or focused/defocused to control the ejection timing, or an external source may be used to extract droplets from the acoustically excited liquid on the surface of the pool on demand. Regardless of the timing mechanism employed, the size of the ejected droplets is determined by the waist diameter of the focused acoustic beam. Acoustic ink printing is attractive because it does not require the nozzles or the small ejection orifices which have caused many of the reliability and pixel placement accuracy problems that conventional drop on demand and

continuous stream ink jet printers have suffered. The size of the ejection orifice is a critical design parameter of an ink jet because it determines the size of the droplets of ink that the jet ejects. As a result, the size of the ejection orifice cannot be increased, without sacrificing resolution.

- 5 Acoustic printing has increased intrinsic reliability because there are no nozzles to clog. As will be appreciated, the elimination of the clogged nozzle failure mode is especially relevant to the reliability of large arrays of ink ejectors, such as page width arrays comprising several thousand separate ejectors. Furthermore, small ejection orifices are avoided, so
- 10 acoustic printing can be performed with a greater variety of inks than conventional ink jet printing, including inks having higher viscosities and inks containing pigments and other particulate components. It has been found that acoustic ink printers embodying printheads comprising acoustically illuminated spherical focusing lenses can print precisely
- 15 positioned pixels (i.e., picture elements) at resolutions which are sufficient for high quality printing of relatively complex images. It has also been discovered that the size of the individual pixels printed by such a printer can be varied over a significant range during operation, thereby accommodating, for example, the printing of variably shaded
- 20 images. Furthermore, the known droplet ejector technology can be adapted to a variety of printhead configurations, including (1) single ejector embodiments for raster scan printing, (2) matrix configured ejector arrays for matrix printing, and (3) several different types of pagewidth ejector arrays, ranging from single row, sparse arrays for
- 25 hybrid forms of parallel/serial printing to multiple row staggered arrays with individual ejectors for each of the pixel positions or addresses within a pagewidth image field (i.e., single ejector/pixel/line) for ordinary line

printing. Inks suitable for acoustic ink jet printing typically are liquid at ambient temperatures (i.e., about 25°C), but in other embodiments the ink is in a solid state at ambient temperatures and provision is made for liquefying the ink by heating or any other suitable method prior to  
5 introduction of the ink into the printhead. Images of two or more colors can be generated by several methods, including by processes wherein a single printhead launches acoustic waves into pools of different colored inks. Further information regarding acoustic ink jet printing apparatus and processes is disclosed in, for example, U.S. Patent  
10 4,308,547, U.S. Patent 4,697,195, U.S. Patent 5,028,937, U.S. Patent 5,041,849, U.S. Patent 4,751,529, U.S. Patent 4,751,530, U.S. Patent 4,751,534, U.S. Patent 4,801,953, and U.S. Patent 4,797,693, the disclosures of each of which are totally incorporated herein by reference. The use of focused acoustic beams to eject droplets of  
15 controlled diameter and velocity from a free-liquid surface is also described in *J. Appl. Phys.*, vol. 65, no. 9 (1 May 1989) and references therein, the disclosure of which is totally incorporated herein by reference.

In acoustic ink printing processes, the printhead produces  
20 approximately 2.2 picoliter droplets by an acoustic energy process. The ink under these conditions preferably displays a melt viscosity of from about 1 to about 25 centipoise at the jetting temperature. In addition, once the ink has been jetted onto the printing substrate, the image thus generated preferably exhibits excellent crease properties, and is  
25 nonsmearing, waterfast, of excellent transparency, and of excellent fix. The vehicle preferably displays a low melt viscosity in the acoustic head while also displaying solid like properties after being jetted onto the

substrate. Since the acoustic head can tolerate temperatures typically up to about 180°C, the vehicle for the ink preferably displays liquid-like properties (such as a viscosity of from about 1 to about 25 centipoise) at a temperature of from about 75 to about 180°C, and solidifies or  
5 hardens after being jetted onto the substrate such that the resulting image exhibits a hardness value of from about 0.1 to about 0.5 millimeter (measured with a penetrometer according to the ASTM penetration method D1321).

Ink jet printing processes that employ inks that are solid at  
10 room temperature and liquid at elevated temperatures are known. For example, U.S. Patent 4,490,731, the disclosure of which is totally incorporated herein by reference, discloses an apparatus for dispensing solid inks for printing on a substrate such as paper. The ink vehicle is chosen to have a melting point above room temperature so that the  
15 ink, which is melted in the apparatus, will not be subject to evaporation or spillage during periods of nonprinting. The vehicle selected possesses a low critical temperature to permit the use of the solid ink in a thermal ink jet printer. In thermal ink jet printing processes employing these phase-change inks, the solid ink is melted by a heater in the printing  
20 apparatus and used as a liquid in a manner similar to that of conventional piezoelectric or thermal ink jet printing. Upon contact with the printing substrate, the molten ink solidifies rapidly, enabling the dye to remain on the surface instead of being carried into the paper by capillary action, thereby enabling higher print density than is generally  
25 obtained with liquid inks. After the phase-change ink is applied to the substrate, freezing on the substrate resolidifies the ink.

In phase-change printing processes, the ink preferably undergoes a change with temperature from a solid state to a liquid state in a desirably short period of time, typically in less than about 100 milliseconds. One advantage of phase-change inks is their ability to  
5 print superior images on plain paper, since the phase-change ink quickly solidifies as it cools, and, since it is primarily waxy in nature, it does not normally soak into a paper medium.

Phase-change inks also preferably exhibit a high degree of transparency, generally measured in terms of haze value of the ink.  
10 Transparent, low haze inks exhibit high gloss and high optical density compared to opaque inks, although both may appear to be evenly colored.

The use of phase-change inks in acoustic ink printing processes is also known. U.S. Patent 4,745,419 (Quate et al.), the disclosure of which is totally incorporated herein by reference, discloses  
15 acoustic ink printers of the type having a printhead including one or more acoustic droplet ejectors for supplying focused acoustic beams. The printer comprises a carrier for transporting a generally uniformly thick film of hot melt ink across its printhead, together with a heating  
20 means for liquefying the ink as it nears the printhead. The droplet ejector or ejectors are acoustically coupled to the ink via the carrier, and their output focal plane is essentially coplanar with the free surface of the liquefied ink, thereby enabling them to eject individual droplets of ink therefrom on command. The ink, on the other hand, is moved  
25 across the printhead at a sufficiently high rate to maintain the free surface which it presents to the printhead at a substantially constant level. A variety of carriers may be employed, including thin plastic and

metallic belts and webs, and the free surface of the ink may be completely exposed or it may be partially covered by a mesh or perforated layer. A separate heating element may be provided for liquefying the ink, or the lower surface of the carrier may be coated with a thin layer of electrically resistive material for liquefying the ink by localized resistive heating.

U.S. Patent 5,541,627 (Quate), the disclosure of which is totally incorporated herein by reference, discloses a method and apparatus for ejecting droplets from the crests of capillary waves riding on the free surface of a liquid by parametrically pumping the capillary waves with electric fields from probes located near the crests. Crest stabilizers are beneficially used to fix the spatial locations of the capillary wave crests near the probes. The probes are beneficially switchably connected to an AC voltage supply having an output that is synchronized with the crest motion. When the AC voltage is applied to the probes, the resulting electric field adds sufficient energy to the system so that the surface tension of the liquid is overcome and a droplet is ejected. The AC voltage is synchronized such that the droplet is ejected about when the electric field is near its minimum value. A plurality of droplet ejectors are arranged and the AC voltage is switchably applied so that ejected droplets form a predetermined image on a recording surface. The capillary waves can be generated on the free surface of the liquid by using acoustical energy at a level approaching the onset of droplet ejection. The liquid used with the invention must also be attracted by an electric field.

Phase-change inks used in acoustic ink printing processes also preferably exhibit a low acoustic-loss value, typically below about



100 decibels per millimeter. In addition, the ink vehicle preferably can fill the pores of a porous substrate, such as paper, and preferably has a melting point of from about 80 to about 120°C; this melting point, along with low acoustic-loss, enables a minimization of energy consumption.

- 5 When the phase-change inks are used in an electric field assisted acoustic ink printing process, the inks also are sufficiently conductive to permit the transmission of electrical signals generated by the electric field assisted acoustic ink jet printer; the inks preferably exhibit a conductivity of from about 2 to about 9 log(picomho/cm) (measured
- 10 under melt conditions at about 150°C by placing an aluminum electrode in the molten ink and reading the resistivity output on a GenRad 1689 precision RLC Digibridge at a frequency of 1 kiloHertz). In general, the conductivity of a material can be measured in terms of the reciprocal of resistivity, which is the capacity for electrical resistance.
- 15 Further information regarding electric field assisted acoustic ink printing processes is disclosed in, for example, Copending Application U.S. Serial No. 09/280,717, filed March 30, 1999, entitled "Method and Apparatus for Moving Ink Drops using an Electric Field and Transfuse Printing System Using the Same," with the named inventors John S. Berkes, Vittorio R.
- 20 Castelli, Scott A. Elrod, Gregory J. Kovacs, Meng H. Lean, Donald L. Smith, Richard G. Stearns, and Joy Roy, the disclosure of which is totally incorporated herein by reference, which discloses a method of forming and moving ink drops across a gap between a printhead and a print medium or intermediate print medium in a marking device. The
- 25 method includes generating an electric field, forming the ink drops adjacent to the printhead, and controlling the electric field. The electric field is generated to extend across the gap. The ink drops are

formed in an area adjacent to the printhead. The electric field is controlled such that an electrical attraction force exerted on the formed ink drops by the electric field is the greatest force acting on the ink drops. The marking device can be incorporated into a transfuse  
5 printing system having an intermediate print medium made of one or more materials that allow for lateral dissipation of electrical charge from the incident ink drops.

U.S. Patent 5,876,492 (Malhotra et al.), the disclosure of which is totally incorporated herein by reference, discloses an ink  
10 comprising (1) a liquid ester vehicle, (2) a solid ester compound, (3) a liquid crystalline ester compound, (4) a UV absorber, (5) an antioxidant, and (6) a colorant.

U.S. Patent 5,922,117 (Malhotra et al.), the disclosure of which is totally incorporated herein by reference, discloses an ink  
15 composition comprising (1) a liquid alcohol vehicle, (2) a solid alcohol compound, (3) a quaternary compound, (4) a lightfastness UV absorber, (5) a lightfastness antioxidant, and (6) a colorant.

U.S. Patent 5,902,390 (Malhotra et al.), the disclosure of which is totally incorporated herein by reference, discloses an ink  
20 comprising (1) a liquid ketone, (2) a solid ketone, (3) a lightfastness UV absorber, (4) a lightfastness antioxidant, and (5) a colorant.

U.S. Patent 5,931,995 (Malhotra et al.), the disclosure of which is totally incorporated herein by reference, discloses an ink  
25 comprising (1) a liquid aldehyde, a liquid acid, or mixtures thereof, (2) a solid additive aldehyde compound, a solid additive acid compound, or mixtures thereof, (3) a lightfastness UV absorber, (4) a lightfastness antioxidant, and (5) a colorant.

Copending Application U.S. Serial No. 08/933,914, entitled "Hot Melt Ink Compositions," filed September 23, 1997, with the named inventors Shadi L. Malhotra and Danielle C. Boils, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) a liquid cyclic vehicle, (2) a cyclic compound, (3) a liquid crystalline nitrile compound, (4) a lightfastness UV absorber, (5) a lightfastness antioxidant, and (6) a colorant.

Copending Application U.S. Serial No. 09/281,571, entitled "Ink Compositions," filed March 30, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, and Raymond W. Wong, the disclosure of which is totally incorporated herein by reference, discloses an ink composition containing (1) a first solid carbamate, (2) a second carbamate with a dissimilar melting point from the first solid carbamate (1), (3) a lightfastness component, (4) a lightfastness antioxidant, and (5) a colorant.

Copending Application U.S. Serial No. 09/362,673, entitled "Inks," filed July 29, 1999, with the named inventors Raymond W. Wong, Marcel P. Breton, Danielle C. Boils, Fatima M. Mayer, and Shadi L. Malhotra, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) a carbamate or thiourea with a melting point of from about 60°C to about 120°C and an acoustic-loss value of from about 25 to about 80 decibels per millimeter, (2) an alcohol compound with a melting point of about 25°C to about 90°C and with an acoustic-loss value of from about 5 to about 40 decibels per millimeter, (3) a lightfastness component, (4) an antioxidant, and (5) a colorant.

Copending Application U.S. Serial No. 09/300,331, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, Raymond W. Wong, Danielle C. Boils, Carl P. Tripp, and Pudupadi R. Sundararajan, the disclosure of which is totally  
5 incorporated herein by reference, discloses an ink composition comprising (1) a solid oxazoline compound with a melting point of from about 60°C to about 120°C and an acoustic-loss value of from about 25 to about 80 decibels per millimeter; (2) a carbamate compound with a melting point of from about 25°C to about 100°C; (3) an alcohol  
10 compound; (4) a lightfastness component; (5) a lightfastness antioxidant; and (6) a colorant.

Copending Application U.S. Serial No. 09/300,193, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Raymond W. Wong, Shadi L. Malhotra, and Marcel P. Breton, the  
15 disclosure of which is totally incorporated herein by reference, discloses a conductive ink composition comprising (1) an acid salt; (2) a conductive quaternary compound; (3) a viscosity modifying compound; (4) a lightfastness component; (5) a lightfastness antioxidant; and (6) a colorant.

Copending Application U.S. Serial No. 09/300,333, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, and Raymond W. Wong, the disclosure of which is totally incorporated herein by reference, discloses an ink  
20 composition containing (1) a solid carbamate compound; (2) an alcohol compound with a melting point of from about 25°C to about 90°C; (3) a lightfastness component; (4) a lightfastness antioxidant; and  
25 (5) a colorant.

Copending Application U.S. Serial No. 09/300,210, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Shadi L. Malhotra, James D. Mayo, and Marcel P. Breton, the disclosure of which is totally incorporated herein by reference, discloses an aqueous ink composition comprising (1) a quaternary compound selected from the group consisting of (a) imidazolinium quaternary salts, (b) phosphonium quaternary salts, and (c) ammonium quaternary salts; (2) a liquid ink vehicle; (3) a paper-curl reducing compound; (4) a lightfastness component; (5) a lightfastness antioxidant; (6) a substantially water soluble organic salt or a substantially water soluble inorganic salt; (7) a biocide; and (8) a colorant.

Copending Application U.S. Serial No. 09/300,332, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, Danielle C. Boils, Raymond W. Wong, Guerino G. Sacripante, and John M. Lennon, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) a mixture of a salt and an oxyalkylene compound wherein the conductive mixture possesses a melting point of from about 60°C to about 120°C; (2) an ink vehicle compound with a melting point of from about 80°C to about 100°C; (3) a viscosity modifying amide compound; (4) a lightfastness component; (5) a lightfastness antioxidant; and (6) a colorant.

Copending Application U.S. Serial No. 09/342,392, entitled "Inks," filed June 29, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, and Raymond W. Wong, the disclosure of which is totally incorporated herein by reference, discloses an ink composition

comprising (1) an azole compound, (2) a viscosity compound, (3) a lightfastness component, (4) an antioxidant, and (5) a colorant.

Copending Application U.S. Serial No. 09/342,947, entitled "Ink Compositions," filed June 29, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, and Gregory J. Kovacs, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) a polymer; (2) an acid compound of the formula  $\text{CH}_3(\text{CH}_2)_m(\text{CH}_2\text{CH}=\text{CH})_p(\text{CH}_2)_n\text{COOH}$  wherein n, m, and p represent the number of segments; (3) a conductive component; (4) a lightfastness component; and (5) a colorant.

Copending Application U.S. Serial No. 09/281,682, entitled "Ink Compositions," filed March 30, 1999, with the named inventors H. Bruce Goodbrand, Danielle C. Boils, Pudupadi R. Sundararajan, Raymond W. Wong, and Shadi L. Malhotra, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) a thiourea with a melting point of from about 60 to about 120°C and with an acoustic-loss value of from about 25 to about 80 decibels per millimeter, (2) an optional ink carbamate with a melting point of from about 25°C to about 60°C and with an acoustic-loss value of from about 5 to about 40 decibels per millimeter, (3) a lightfastness component, (4) a lightfast antioxidant, and (5) a colorant.

Copending Application U.S. Serial No. 09/300,373, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Marcel P. Breton, Shadi L. Malhotra, and Raymond W. Wong, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) a solid urea compound; (2) an alcohol; (3)

a lightfastness component; (4) a lightfast antioxidant; and (5) a colorant.

Copending Application U.S. Serial No. 09/300,298, entitled "Ink Compositions," filed April 27, 1999, with the named inventors Shadi L. Malhotra, Raymond W. Wong, and Marcel P. Breton, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (1) an oxazoline compound; (2) a thiourea compound with an optional melting point of from about 25 to about 100°C and with an optional acoustic-loss value of from about 5 to about 40 decibels per millimeter; (3) an alcohol; (4) a lightfastness compound; (5) an antioxidant; and (6) a colorant.

Copending Application U.S. Serial No. <sup>09/404,569</sup>~~(not yet assigned;~~  
~~Attorney Docket No. D/99432)~~, entitled "Conductive Inks Containing Pyridine Compounds," filed concurrently herewith, with the named inventors Shadi L. Malhotra, Raymond W. Wong, and Marcel P. Breton, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (a) an ink vehicle which comprises a conductive pyridinium compound having a melting point of no lower than about 60°C and no higher than about 155°C, (b) a viscosity modifier which is a pyridine compound, a pyrimidine compound, a pyrazine compound, a pyridazine compound, or mixtures thereof, said pyridine, pyrimidine, pyrazine, or pyridazine compounds having a melting point of no lower than about 60°C and no higher than about 155°C, (c) a binder which is a polymeric pyridine or pyridinium compound; (d) a colorant, (e) an optional antioxidant, and (f) an optional UV absorber.

09/401,249  
Copen ding Application U.S. Serial No. (not yet assigned;

~~Attorney Docket No. D/99434~~), entitled "Conductive Inks Containing Sulfonate Salts," filed concurrently herewith, with the named inventors Shadi L. Malhotra, Raymond W. Wong, and Marcel P. Breton, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (a) an ink vehicle which is selected from (i) 1,3-dialkyl ureas, (ii) N,N'-ethylene bisalkylamides, (iii) N-[4-chloro-3-[4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-ylamino]phenyl]-2-(1-octadecenyl) succinimide, (iv) 1,3-diamino-5,6-bis(octyloxy) isoindoline, (v) N,N-dimethyl alkylamine N-oxides, (vi) alkyl amides, or (vii) mixtures thereof, said ink vehicle having a melting point of no lower than about 60°C and no higher than about 155°C, (b) a viscosity modifier which is an amide having a melting point of no lower than about 60°C and no higher than about 155°C, (c) a conductive sulfonate salt having a melting point of no lower than about 60°C and no higher than about 155°C, (d) a colorant, (e) an optional antioxidant, and (f) an optional ultraviolet absorber.

09/404,425  
Copen ding Application U.S. Serial No. (not yet assigned;

~~Attorney Docket No. D/99530~~), entitled "Hot Melt Inks Containing Polyanhydrides," filed concurrently herewith, with the named inventor Shadi L. Malhotra, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (a) a polyanhydride ink vehicle, (b) a nonpolymeric anhydride viscosity modifier, and (c) a colorant.

Copen ding Application U.S. Serial No. (not yet assigned; Attorney Docket No. D/99531), entitled "Hot Melt Inks Containing Aldehyde Copolymers," filed concurrently herewith, with the named



inventor Shadi L. Malhotra, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (a) an aldehyde copolymer ink vehicle, (b) a nonpolymeric aldehyde viscosity modifier, (c) a colorant, (d) an optional conductivity enhancing agent, (e) an optional antioxidant, and (f) an optional UV absorber.

6 Copending Application U.S. Serial No. <sup>09/401,226</sup> ~~(not yet assigned; Attorney Docket No. D/99541)~~, entitled "Hot Melt Inks Containing Polyketones," filed concurrently herewith, with the named inventor  
10 Shadi L. Malhotra, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (a) a nonpolymeric ketone ink vehicle having a melting point of at least about 60°C, (b) a polyketone hardening component, (c) a colorant, (d) a conductivity enhancing agent, (e) an optional antioxidant, (f) an  
15 optional viscosity modifier which is a nonpolymeric carbonate, monoketone, or diketone, and (g) an optional ultraviolet absorber.

Copending Application U.S. Serial No. <sup>09/401,250</sup> ~~(not yet assigned; Attorney Docket No. D/99542)~~, entitled "Hot Melt Inks Containing Polyesters," filed concurrently herewith, with the named inventor Shadi  
20 L. Malhotra, the disclosure of which is totally incorporated herein by reference, discloses an ink composition comprising (a) a polyester ink vehicle, (b) a nonpolymeric ester viscosity modifier, (c) a colorant, (d) an optional colorant dispersing agent, (e) an optional conductivity enhancing agent, (f) an optional antioxidant, and (g) an optional UV  
25 absorber.

While known compositions and processes are suitable for their intended purposes, a need remains for improved phase-change

inks. In addition, a need remains for improved inks for acoustic ink printing. Further, a need remains for conductive inks. Additionally, a need remains for phase-change inks with desirable melting point values. There is also a need for phase-change inks with melt viscosities

5 at jetting temperatures that enable high quality ink jet printing. In addition, there is a need for phase-change inks that generate images with excellent hardness values. Further, there is a need for phase-change inks undergo, upon heating, a change from a solid state to a liquid state in a desirably rapid period of time. Additionally, there is a

10 need for phase-change inks with acoustic-loss values that are desirable for acoustic ink printing applications. A need also remains for phase-change ink compositions with conductivity values that are desirable for electric field assisted acoustic ink printing processes. In addition, a need remains for phase-change inks that generate images with

15 desirably low haze values. Further, a need remains for phase-change inks that generate images with good crease resistance. Additionally, a need remains for phase-change inks that generate images with high gloss. There is also a need for hot melt ink compositions having ink vehicles in which dye colorants are highly soluble, thereby enabling

20 prints with desirably high optical density using smaller amounts of the ink, and enabling thinner images of the ink on the substrate (for example, a printing ink thickness of 5 microns, compared to 10 microns). In addition, there is a need for phase-change inks that generate images with excellent scratch resistance.

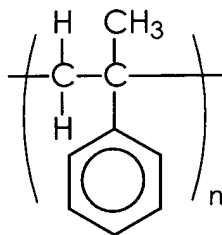
25

## SUMMARY OF THE INVENTION

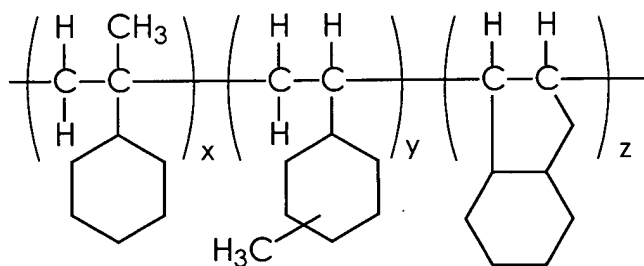
The present invention is directed to an ink composition comprising (a) a styrene polymer or terpene polymer hardening component, (b) a nonpolymeric aromatic viscosity modifier, (c) a colorant, (d) an optional nonpolymeric aromatic ink vehicle, (e) an optional colorant dispersing agent, (f) an optional conductivity enhancing agent, (g) an optional antioxidant, and (h) an optional UV absorber.

## DETAILED DESCRIPTION OF THE INVENTION

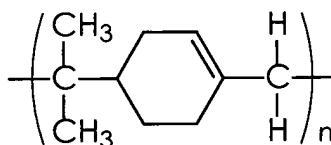
The inks of the present invention contain a styrene polymer or a terpene polymer hardening component. The styrene polymer can be either a styrene homopolymer or a styrene copolymer. Examples of suitable styrene polymers include (1) poly ( $\alpha$ -methyl styrene), of the formula



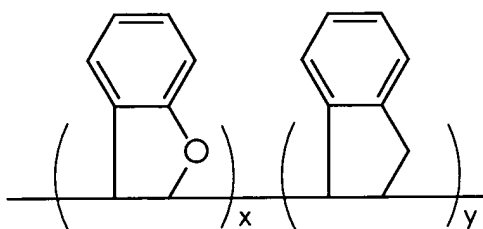
( $M_n=685$ ; Aldrich 19,182-5;  $M_n=790$ ; Aldrich 19,183-3; hardness value 92), (2) poly (vinyl toluene-co- $\alpha$ -methyl styrene) (Aldrich 45,722-1; 45,724-1; hardness value 90), (3) poly (methyl styrene-co-indene) hydrogenated, of the formula



( $M_n=750$ ;  $T_g=72$ ; Aldrich 45,722-1; hardness value 92), (4) poly (styrene-co-allyl alcohol) ( $M_n=1200$ ; 60 mole percent styrene; Aldrich 46,813-4; hardness value 91.6;  $M_n=1600$ ; 60 mole percent styrene; Aldrich 19,110-8), and the like, as well as mixtures thereof. Examples of suitable polyterpenes include (1) polylimonene (Aldrich 45,755-8; hardness value 84.8), (2) poly- $\beta$ -pinene, of the formula



(Aldrich 45,752-3; hardness value 85.8), (3) poly(coumarone-co-indene), of the formula



( $M_n=735$ ; Aldrich 44,668-8;  $M_n=1090$ ; Aldrich 44,669-6; hardness value 92), and the like, as well as mixtures thereof. The styrene polymer or polyterpene hardening component is present in the ink in any desired or effective amount, typically no less than about 0.5 percent by weight of the ink, and preferably no less than about 5 percent by weight of the ink,

and typically no more than about 99 percent by weight of the ink, preferably no more than about 28 percent by weight of the ink, and more preferably no more than about 20 percent by weight of the ink, although the amount can be outside of these ranges. The styrene polymer or polyterpene hardening component typically has a melting point of no lower than about 60°C, preferably no lower than about 65°C, and more preferably no lower than about 70°C, and typically has a melting point of no higher than about 155°C, preferably no higher than about 135°C, and more preferably no higher than about 100°C, although the melting point can be outside of these ranges, and typically has a hardness value of at least about 80, although the hardness value can be outside of this range.

The inks of the present invention further contain a nonpolymeric aromatic viscosity modifier. Examples of suitable nonpolymeric aromatic viscosity modifiers include (a) biphenyl compounds, such as (1) biphenylene (Aldrich 32,195-8), (2) 4-acetylbiphenyl (Aldrich 12,272-6), (3) 2-biphenyl carboxylic acid (Aldrich B3,470-2), (4) 2,2'-biphenyldimethanol (Aldrich 32,975-4), (5) 4,4'-dimethyl biphenyl (Aldrich D15,120-3), (6) 2,2'-bis (bromomethyl)-1,1'-biphenyl (Aldrich 33,064-7), (7) 4,4'-bis (dimethylamino) biphenyl carbinol (Aldrich 85,855-2), (8) 4-bromo biphenyl (Aldrich 28,199-9), (9) diphenylfulvene (Aldrich D20,770-5), (10) diphenyl sulfone (Aldrich P3,535-9), (11) 1,2-diphenoxy ethane (Aldrich 14,028-7), (12) triphenyl methane (Aldrich 10,130-3; hardness value 76.4), and the like, as well as mixtures thereof, (b) fluorene compounds, such as (1) fluorene (Aldrich 41,819-6), (2) 9-fluorene methanol (Aldrich 16,050-4), (3) 9-fluorene acetic acid (Aldrich 32,889-8), (4) 3-amino fluoranthene (Aldrich A5,540-3), (5) 1-amino

fluorene (Aldrich 29,977-4), (6) 2-amino fluorene (Aldrich A5,550-0), (7) 9-bromo-9-phenylfluorene (Aldrich 36,887-3), (8) 1-methyl fluorene (Aldrich M4,659-4), (9) methyl-9-fluorenylidene acetate (Aldrich 40,004-1), (10) 4,4'-(9-fluorenylidene) bis(2-phenoxy ethanol) (Aldrich 43,792-1), (11) N-(9-fluorenyl methoxy carbonyl)-L-valinol (Aldrich 44,567-3), (12) 9-fluorenone (Aldrich F,150-6), and the like, as well as mixtures thereof, (c) phenanthrene compounds, such as (1) phenanthrene (Aldrich P1,140-9; hardness value 73.8), (2) 9-iodophenanthrene (Aldrich 38,935-8), (3) 9-acetylphenanthrene (Aldrich A1,960-1), (4) 9-amino phenanthrene (Aldrich 14,910-1), and the like, as well as mixtures thereof, (d) pyrene compounds, such as (1) 1-amino pyrene (Aldrich A7,790-3), (2) 1-acetylpyrene (Aldrich 39,142-8), (3) 1-bromopyrene (Aldrich 39,157-3), (4) 1-(bromoacetyl) pyrene (Aldrich 39,440-8), (5) 1,2,3,6,7,8-hexahydropyrene (Aldrich H960-5), (6) 1-pyrenemethanol (Aldrich 38,943-9), (7) 1-pyrenebutanol (Aldrich 39,965-5), and the like, as well as mixtures thereof, (e) adamantane compounds, such as (1) 1-adamantane methanol (Aldrich 18,420-9), (2) 1-adamantane ethanol (Aldrich 18,811-5), (3) 1-bromo adamantane (Aldrich 10,922-3), (4) 2-bromo adamantane (Aldrich 15,383-4), (5) 1-iodo adamantane (Aldrich 37,719-8), (6) 2-(1-adamantyl)-4-methyl phenol (Aldrich 39,468-8), (7) 1-bromo-3-(bromomethyl) adamantane (Aldrich 40,315-6), (8) 1-bromo-3,5-dimethyl adamantane (Aldrich 18,784-4), (9) 3-(bromomethyl)-2,4,10-trioxadamantane (Aldrich 36,721-4), (10) 1,3-dibromoadamantane (Aldrich 40,308-3), (11) 1,4-dibromo adamantane (Aldrich 41,273-2), (12) dimethyl-1,3-adamantane dicarboxylate (Aldrich 34,083-9), (13) 1-azido adamantane (Aldrich 27,621-9), (14) 3-noradamantane carboxylic acid (Aldrich 27,623-5), (15) 1-adamantyl bromomethyl ketone (Aldrich 14,929-

2), and the like, as well as mixtures thereof, (f) dibenzo compounds, such as (1) dibenzo-24-crown-8 (Aldrich 25,319-7), (2) dibenzo-30-crown-10 (Aldrich 33,251-8), (3) dibenzofuran (Aldrich 33,251-8), (4) dibenzosuberane (Aldrich D10,495-7), (5) dibenzosuberanol (Aldrich D3,172-9), (6) dibenzosuberol (Aldrich D10,497-3), (7) dibenzosuberone (Aldrich D3,173-7; hardness value 85.2), (8) dibenzothiophene (Aldrich 43,330-6), (9) diphenylfulvene (Aldrich D20,770-5), (10) 1,3-diphenyl isobenzofuran (Aldrich 10,548-1; hardness value 62), and the like, as well as mixtures thereof, (g) diphenyl phosphino compounds, such as (1) bis(diphenylphosphino) methane (Aldrich 12,756-6), (2) 1,2-bis(diphenylphosphino) ethane (Aldrich 10,649-6), (3) cis-1,2-bis(diphenylphosphino) ethylene (Aldrich 32,764-6), (4) trans-1,2-bis(diphenylphosphino) ethylene (Aldrich 28,797-0), (5) 1,4-bis(diphenylphosphino) butane (Aldrich 26,194-7), (6) (2R,3R)-(+)-bis(diphenylphosphino) butane (Aldrich 34,793-0), (7) (2S,3S)-(-)-bis(diphenylphosphino) butane (Aldrich 25,909-8), (8) 1,6-bis(diphenyl phosphino) hexane (Aldrich 28,798-9), (9) 1,1,1-tris(diphenyl phosphino methyl) ethane (Aldrich 38,074-1), (10) 1,4-bis(dicyclohexyl phosphino) butane (Aldrich 44,042-6), and the like, as well as mixtures thereof, (h) phenylsulfonyl compounds, such as (1) cis-1,2-bis(phenylsulfonyl) ethylene (Aldrich 25,853-9), (2) bis(phenylsulfonyl) methane (Aldrich 30,296-1), (3) 1-bromomethyl-2-((phenylsulfonyl) methyl) benzene (Aldrich 30,412-3), (4) 2-(phenylsulfonyl)tetrahydropyran (Aldrich 31,748-9), and the like, as well as mixtures thereof. The viscosity modifier generally acts to lower the viscosity of the ink at the jetting temperature, typically lowering the viscosity by from about 10 to about 20 centipoise compared to a similar composition containing no viscosity modifier, although the





Permanent Violet VT 2645 (Paul Uhlich); Heliogen Green L8730 (BASF); Argyle Green XP-111-S (Paul Uhlich); Brilliant Green Toner GR 0991 (Paul Uhlich); Lithol Scarlet D3700 (BASF); Toluidine Red (Aldrich); Scarlet for Thermoplast NSD PS PA (Ugine Kuhlmann of Canada); E.D. Toluidine Red (Aldrich); Lithol Rubine Toner (Paul Uhlich); Lithol Scarlet 4440 (BASF); Bon Red C (Dominion Color Company); Royal Brilliant Red RD-8192 (Paul Uhlich); Oracet Pink RF (Ciba-Geigy); Paliogen Red 3871K (BASF); Paliogen Red 3340 (BASF); Lithol Fast Scarlet L4300 (BASF); Heliogen Blue L6900, L7020 (BASF); Heliogen Blue K6902, K6910 (BASF); Heliogen Blue D6840, D7080 (BASF); Sudan Blue OS (BASF); Neopen Blue FF4012 (BASF); PV Fast Blue B2G01 (American Hoechst); Irgalite Blue BCA (Ciba-Geigy); Paliogen Blue 6470 (BASF); Sudan III (Red Orange) (Matheson, Coleman Bell); Sudan II (Orange) (Matheson, Coleman Bell); Sudan Orange G (Aldrich), Sudan Orange 220 (BASF); Paliogen Orange 3040 (BASF); Ortho Orange OR 2673 (Paul Uhlich); Paliogen Yellow 152, 1560 (BASF); Lithol Fast Yellow 0991K (BASF); Paliotol Yellow 1840 (BASF); Novoperm Yellow FGL (Hoechst); Permanent Yellow YE 0305 (Paul Uhlich); Lumogen Yellow D0790 (BASF); Suco-Yellow L1250 (BASF); Suco-Yellow D1355 (BASF); Suco Fast Yellow D1355, D1351 (BASF); Hostaperm Pink E (American Hoechst); Fanal Pink D4830 (BASF); Cinquasia Magenta (Du Pont); Paliogen Black L0084 (BASF); Pigment Black K801 (BASF); and carbon blacks such as REGAL 330® (Cabot), Carbon Black 5250, Carbon Black 5750 (Columbia Chemical), and the like.

Examples of suitable dyes include Pontamine; Food Black 2; Carodirect Turquoise FBL Supra Conc. (Direct Blue 199), available from Carolina Color and Chemical; Special Fast Turquoise 8 GL Liquid (Direct Blue 86), available from Mobay Chemical; Intrabond Liquid Turquoise GLL

(Direct Blue 86), available from Crompton and Knowles; Cibracron Brilliant Red 38-A (Reactive Red 4), available from Aldrich Chemical; Drimarene Brilliant Red X-2B (Reactive Red 56), available from Pylam, Inc.; Levafix Brilliant Red E-4B, available from Mobay Chemical; Levafix Brilliant Red E6-BA, available from Mobay Chemical; Procion Red H8B (Reactive Red 31), available from ICI America; Pylam Certified D&C Red #28 (Acid Red 92), available from Pylam; Direct Brill Pink B Ground Crude, available from Crompton and Knowles; Cartasol Yellow GTF Presscake, available from Sandoz, Inc.; Tartrazine Extra Conc. (FD&C Yellow #5, Acid Yellow 23), available from Sandoz, Inc.; Carodirect Yellow RL (Direct Yellow 86), available from Carolina Color and Chemical; Cartasol Yellow GTF Liquid Special 110, available from Sandoz, Inc.; D&C Yellow #10 (Acid Yellow 3), available from Tricon; Yellow Shade 16948, available from Tricon; Basacid Black X 34, available from BASF; Carta Black 2GT, available from Sandoz, Inc.; and the like. Particularly preferred are solvent dyes; within the class of solvent dyes, spirit soluble dyes are preferred because of their compatibility with the ink vehicles of the present invention. Examples of suitable spirit solvent dyes include Neozapon Red 492 (BASF); Orasol Red G (Ciba-Geigy); Direct Brilliant Pink B (Crompton & Knowles); Aizen Spilon Red C-BH (Hodogaya Chemical); Kayanol Red 3BL (Nippon Kayaku); Levanol Brilliant Red 3BW (Mobay Chemical); Levaderm Lemon Yellow (Mobay Chemical); Spirit Fast Yellow 3G; Aizen Spilon Yellow C-GNH (Hodogaya Chemical); Sirius Supra Yellow GD 167; Cartasol Brilliant Yellow 4GF (Sandoz); Pergasol Yellow CGP (Ciba-Geigy); Orasol Black RLP (Ciba-Geigy); Savinyl Black RLS (Sandoz); Dermacarbon 2GT (Sandoz); Pyrazol Black BG (ICI); Morfast Black Conc. A (Morton-Thiokol); Diaazol Black RN Quad (ICI); Orasol Blue

GN (Ciba-Geigy); Savinyl Blue GLS (Sandoz); Luxol Blue MBSN (Morton-Thiokol); Sevron Blue 5GMF (ICI); Basacid Blue 750 (BASF), and the like. Neozapon Black X51 [C.I. Solvent Black, C.I. 12195] (BASF), Sudan Blue 670 [C.I. 61554] (BASF), Sudan Yellow 146 [C.I. 12700] (BASF), and Sudan  
5 Red 462 [C.I. 26050] (BASF) are preferred.

The inks of the present invention also optionally contain a nonpolymeric aromatic ink vehicle. Examples of suitable nonpolymeric aromatic compounds include (1) 4-hexyl resorcinol (Aldrich 20,946-5), (2) 4-dodecyl resorcinol (Aldrich D22,260-7), (3) 4-(tert-octyl) phenol (Aldrich  
10 29,082-3), (4) 4-bromo-N-dodecyl-1-hydroxy-2-naphthalene carboxamide (Aldrich 37,157-2), (5) 2,2-diphenyl-1,4-diazaspiro-(4,5)deca-1,3-diene (Aldrich 37,146-7), (6) N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Aldrich 29,472-1), (7) 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (Aldrich 43,201-6), (8) 1,4,4a,8a-  
15 tetrahydro-endo-1,4-methanonaphthalene (Aldrich 34,180-0), (9) 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene (Aldrich 10,915-0), (10) 2,5-difluorophenylhydrazine (Aldrich 32,419-1), and the like, as well as mixtures thereof. The ink vehicle typically has a melting point of from about no less than about 60°C, preferably no less than about 65°C, and  
20 more preferably no less than about 70°C, typically has a melting point of no more than about 135°C, preferably no higher than about 130°C, and more preferably no higher than about 100°C, although the melting point can be outside of these ranges. When present, the ink vehicle is present in the ink in any desired or effective amount, typically no less  
25 than about 0.5 percent by weight of the ink, and preferably no less than about 15 percent by weight of the ink, and typically no more than about 98 percent by weight of the ink, preferably no more than about

70 percent by weight of the ink, and more preferably no more than about 50 percent by weight of the ink, although the amount can be outside of these ranges. Preferably, the ink vehicle has an acoustic-loss value of no more than about 100 decibels per millimeter, although the  
5 acoustic-loss value can be outside of this range.

The inks of the present invention optionally contain a colorant dispersing agent. When the colorant is a dye, the colorant dispersing agent is generally a solid dye solvent. When the colorant is a pigment, the colorant dispersing agent is generally a solid pigment  
10 dispersant. Polyaromatics and monomeric aromatic compounds can be difficult to color in the molten state. An ink containing ingredients that originate exclusively from the aromatic family may, on melting, yield a heterogeneous dispersion of the colorant in the aromatic blend. To convert these heterogeneous blends into homogeneous solutions, a  
15 colorant dispersant such as a solid ketone (monomeric or polymeric), solid aldehyde (monomeric or polymeric), solid carbonate (monomeric or polymeric), or solid acid (monomeric or polymeric) that stays with the ink composition and becomes an integral part of the ink can be included in the composition. Alternatively, a liquid solvent can be  
20 employed during the ink formulation process, such as methyl ethyl ketone, acetone, 2-butanone, cyclobutanone, cyclohexanone, or the like, which solvent can later be removed from the ink composition, recovered, and recycled. An advantage of a removable liquid solvent over a nonremovable solid colorant dispersing agent is that inks without  
25 solid colorant dispersing agents therein generally tend to have lower haze values (typically from about 5 to about 10, compared to typical haze values of from about 10 to about 20 for inks containing solid

colorant dispersing agents) after removal of the liquid solvent. The additional step of solvent recovery, however, increases the cost of such inks to a significantly greater extent than the inclusion of a solid colorant dispersing agent.

- 5                    Examples of suitable colorant dispersing agents include materials with a melting point of at least about 60°C, preferably at least about 80°C, and more preferably at least about 100°C, and include (a) organic acids, such as (1) 2-hydroxyisocaproic acid (Aldrich 21,981-9), (2) 2-hydroxy isobutyric acid (Aldrich 16,497-6), (3) benzylmalonic acid  
10 (Aldrich 10,077-3), (4) dibenzoyl-L-tartaric acid monohydrate (Aldrich 13,803-7), (5) methylsuccinic acid (Aldrich M8,120-9), (6) 2-ethyl-2-methylsuccinic acid (Aldrich 15,121-1), (7) 2,2-dimethyl glutaric acid (Aldrich 20,526-5), (8) 3,3-dimethylglutaric acid (Aldrich D15,940-9; hardness value 81.2), (9) (1-hydroxy-1-cyclopropane carboxylic acid  
15 (Aldrich 29,388-1), (10) 2,2,3,3-tetramethyl cyclopropane carboxylic acid (Aldrich 30,156-6), (11) 1-benzo cyclobutane carboxylic acid (Aldrich 32,488-4), (12) 3-oxo-1-indan carboxylic acid (Aldrich 41,077-2), (13) 2-oxo-6-pentyl-2H-pyran-3-carboxylic acid (Aldrich 27,369-4), and the like, as well as mixtures thereof, (b) nonpolymeric ketones, such as (1)  
20 diphenyl carbonate (Aldrich D20,653-9), (2) 1,2-diphenylvinylene carbonate (Aldrich 24,583-6), (3) 2-oxazolidone (Aldrich O-940-9), (4) flavone (Aldrich F60-2), (5) 4-methoxy chalcone (Aldrich 15,758-9; hardness value 70.2), (6) 4'-methoxy chalcone (Aldrich 15,746-5; hardness value 83.5), (7)  $\gamma$ -(2-naphthyl)- $\gamma$ -butyrolactone (Aldrich 40,177-3), (8)  
25 diphenyl- $\gamma$ -butyrolactone (Aldrich 18,320-2; hardness value 75), (9) 2,6-dimethyl-4H-pyran-4-one (Aldrich D18,340-7), (10) distyryl ketone (obtained from ICN Biomedicals; ICN #209984), (11) 4-(4-hydroxyphenyl)-

- 2-butanone (Aldrich 17,851-9; hardness value 75.4), (12) 1,3-diacetyl-2-imidazolidinone (Aldrich 34,078-2), (13) 2,6-diphenyl cyclohexanone (Aldrich 42,471-4), (14) flavanone (Aldrich 10,203-2), (15) 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (Aldrich 41,739-4), (16) 1-(2-hydroxy-5-methylphenyl)-3-phenyl-1,3-propanedione (Aldrich 41,740-8), (17) tetramethyl-1,3-cyclobutanedione (Aldrich T2,100-84), (18) 2,5-oxazolidinedione (Aldrich 36,977-2), (19) 5,5-dimethyloxazolidine-2,4-dione (Aldrich 21,900-2), (20) 3,6-dimethyl-1,4-dioxane-2,5-dione (Aldrich 30,314-3), (21) 2,2-dimethyl-1,3-dioxane-4,6-dione (Aldrich 21,014-5), (22) 4,4-dimethyl-1,3-cyclohexanedione (Aldrich 34,125-8), (23) benzylphenyl ketone (ICN #202318), (24) di-n-benzyl ketone (ICN #208157), (25) diphenyl acetone (ICN #208157; ICN #206354), and the like, as well as mixtures thereof, (c) polymeric ketones, such as (1) poly (vinyl phenyl ketone) ( $T_g=58^\circ\text{C}$ ; Aldrich 43,481-7; hardness value 93.8), (2) poly (vinyl phenyl ketone) hydrogenated (Aldrich 43,482-5; hardness value 94), (3) polycyclohexanone ( $M_n=900$ ;  $T_g=49^\circ\text{C}$ ; Aldrich 46,854-1; hardness value 93.1), (4) poly(coumarone-co-indene) ( $M_n=735$ ; Aldrich 44,668-8;  $M_n=1090$ ; Aldrich 44,669-6; hardness value 92), (5) polycaprolactone ( $M_n=10,000$ ; melting point  $60^\circ\text{C}$ ; Aldrich 44,075-2; hardness value 86), (6) poly(ethylene-co-carbon monoxide) ( $M_n=3000$ ; melting point  $90^\circ\text{C}$ ; viscosity at  $140^\circ\text{C}$  230 centipoise; Aldrich 42,835-3), (7) poly(1-vinylpyrrolidone)-graft-(1-triacontene) ( $T_g=46^\circ\text{C}$ ; Aldrich 43,052-8; hardness value 80), and the like, as well as mixtures thereof, (d) benzaldehyde compounds, such as (1) 3-hydroxybenzaldehyde (Aldrich H1,980-8), (2) 4-hydroxybenzaldehyde (Aldrich 14,408-8), (3) 4-benzyloxybenzaldehyde (Aldrich 12,371-4), (4) 2-carboxybenzaldehyde (Aldrich 11,106-7), (5) 4-nitrobenzaldehyde (Aldrich 13,017-6), (6) 2,3-

dihydroxybenzaldehyde (Aldrich 18,983-9), (7) 2,5-  
 dihydroxybenzaldehyde (Aldrich D10,820-0), (8) 3-hydroxy-4-  
 methoxybenzaldehyde (Aldrich 14,368-5), (9) 4-hydroxy-3-  
 methoxybenzaldehyde (Aldrich V,110-4; hardness value 74.5), (10) 4-  
 5 hydroxy-3-ethoxybenzaldehyde (Aldrich 12,809-0), (11) 4-hydroxy-3-  
 methylbenzaldehyde (Aldrich 31,691-1), (12) 2-hydroxy-5-  
 nitrobenzaldehyde (Aldrich 27,535-2), (13) 3-hydroxy-4-  
 nitrobenzaldehyde (Aldrich 15,616-7), (14) 4-hydroxy-3-  
 nitrobenzaldehyde (Aldrich 14,432-0), (15) 3,4-dibenzyloxy  
 10 benzaldehyde (Aldrich D3,600-3), (16) 3,5-dibenzyloxybenzaldehyde  
 (Aldrich 36,810-5), (17) 4-acetoxy-3,5-dimethoxybenzaldehyde (Aldrich  
 38,774-6; hardness value 79.5), (18) 2-amino-3,5-dibromobenzaldehyde  
 (Aldrich 46,346-9), (19) 2-benzyloxy-4,5-dimethoxybenzaldehyde  
 (Aldrich 42,490-0), (20) 5-bromo-2-hydroxy-3-methoxybenzaldehyde  
 15 (Aldrich 41,047-0), (21) 4-hydroxy-3,5-dimethoxybenzaldehyde (Aldrich  
 S,760-2), (22) 2,3,5-trichlorobenzaldehyde (Aldrich 29, 233-8), (23) 2,3,6-  
 trichlorobenzaldehyde (Aldrich 29,231-1), (24) 2,4,5-  
 trimethoxybenzaldehyde (Aldrich 13,215-2), (25) 2,4,6-  
 trimethoxybenzaldehyde (Aldrich 13,871-1), (26) 3,5-dichloro-2-  
 20 hydroxybenzaldehyde (Aldrich 26,181-5), (27) 3,5-dibromo-2-  
 hydroxybenzaldehyde (Aldrich 12,213-0), (28) 3,5-diiodo-2-  
 hydroxybenzaldehyde (Aldrich 28,344-4), (29) 3,4-dihydroxy-5-  
 methoxybenzaldehyde (Aldrich 46,412-0), (30) 3,5-dimethyl-4-  
 hydroxybenzaldehyde (Aldrich 14,039-2), (31) 2,6-  
 25 dimethoxybenzaldehyde (Aldrich 29,250-8), and the like, as well as  
 mixtures thereof, (e) cinnamaldehydes, such as (1) trans-2-nitro  
 cinnamaldehyde (Aldrich N1,620-7), (2) trans-4-(diethylamino)

cinnamaldehyde (Aldrich 33,849-4), (3) 4-acetoxy-3-methoxy  
cinnamaldehyde (Aldrich 42,754-3), (4) 4-hydroxy-3-methoxy  
cinnamaldehyde (Aldrich 38,205-1), and the like, as well as mixtures  
thereof, (f) other aldehydes, such as (1) 2-hydroxy-1-naphthaldehyde  
5 (Aldrich H4,535-3), (2) 2-methoxy-1-naphthaldehyde (Aldrich 15,134-3),  
(3) 9-anthraldehyde (Aldrich 27,868-8), (4) 5-bromo-2-furaldehyde  
(Aldrich 43,398-5), (5) 5-nitro-2-thiophene carboxaldehyde (Aldrich  
30,229-5), (6) 9-ethyl-3-carbazole carboxaldehyde (Aldrich 15,148-3), (7)  
trans-4-stilbenecarboxaldehyde (Aldrich 26,813-5), (8) 2-hydroxy-5-  
10 methyl-1,3-benzene dicarboxaldehyde (Aldrich 39,385-1), (9) terephthal  
dicarboxaldehyde (Aldrich T220-7; hardness value 73), (10) 2-  
(diphenylphosphino) benzaldehyde (Aldrich 32,620-8), (11) 1-  
(phenylsulfonyl)-2-pyrrolecarboxaldehyde (Aldrich 43,884-7), (12) 1-  
pyrene carboxaldehyde (Aldrich 14,403-7), (13) phenanthrene  
15 carboxaldehyde (Aldrich P1,160-3), (14) 2-fluorene carboxaldehyde  
(Aldrich 15,014-2), and the like, as well as mixtures thereof, (g) polymeric  
aldehydes, such as (1) poly ((phenyl glycidyl ether)-co-formaldehyde)  
( $M_n=570$ ; Aldrich 40,676-7), (2) poly ((o-cresyl glycidyl ether)-co-  
formaldehyde) ( $M_n=870$ ; melting point 70-75°C; Aldrich 40,551-5;  
20 hardness value 92), (3) poly (p-toluenesulfonamide-co-formaldehyde)  
(Aldrich 28,076-3; hardness value 90), and the like, as well as mixtures  
thereof. When a combination of a polymeric and a monomeric  
colorant dispersing agent are present, such as a nonpolymeric  
aldehyde and a polymeric aldehyde, the ratio of polymeric compound  
25 to nonpolymeric compound by weight preferably is from about 0.1:1 to  
about 0.5:1, although the relative amounts can be outside of this range.  
When present, the colorant dispersing agent is present in the ink in any



desired or effective amount, typically no less than about 1 percent by weight of the ink, and typically no more than about 98 percent by weight of the ink, preferably no more than about 50 percent by weight of the ink, more preferably no more than about 35 percent by weight of the ink, and even more preferably no more than about 20 percent by weight of the ink, although the amount can be outside of these ranges.

The inks of the present invention further optionally contain a conductivity enhancing agent when conductive inks are desirable, as in applications such as electric field assisted hot melt acoustic ink printing processes. Any desired or effective conductivity enhancing agent can be employed. Specific examples of suitable conductivity enhancing agents include (1) p-toluene sulfonyl chloride (Aldrich 24,087-7), (2) o-toluene sulfonyl chloride (Aldrich 15,971-9), (3) 1-(p-toluene sulfonyl) imidazole (Aldrich 24,424-4), (4) 1-(p-toluene sulfonyl)-3-nitro-1,2,4-triazole (Aldrich 24,417-1), (5) 2,4,6-triisopropyl benzene sulfonyl chloride (Aldrich 11,949-0), (6) 1-(2,4,6-triisopropyl benzene sulfonyl) imidazole (Aldrich 40,948-0), (7) 1-(2,4,6-triisopropyl benzene sulfonyl)-3-nitro-1,2,4-triazole (Aldrich 40,948-0), (8) 4-nitrobenzene sulfonyl chloride (Aldrich 27,224-8), (9) methyl-1-adamantane sulfonate (Aldrich 40,956-1), (10) octadecyl-4-chlorobenzene sulfonate (Aldrich 47,799-0), (11) tetrabutylammonium trifluoromethanesulfonate (Aldrich 34,509-1), (12) S,S'-ethylene-p-toluene thiosulfonate (Aldrich 23,257-2), (13) pyridinium 3-nitrobenzene sulfonate (Aldrich 27,198-5), and the like, as well as mixtures thereof. The conductivity enhancing agent, when present, is present in the ink in any desired or effective amount, typically no less than about 0.5 percent by weight of the ink, and preferably no less than about 10 percent by weight of the ink, and typically no more

than about 98 percent by weight of the ink, preferably no more than about 30 percent by weight of the ink, and more preferably no more than about 25 percent by weight of the ink, although the amount can be outside of these ranges. The conductivity enhancing agent typically  
5 has a conductivity of at least about 6.0 log(picomho/cm), although the conductivity can be outside of this range.

The optional antioxidants in the ink compositions protect the images from oxidation and also protect the ink components from oxidation during the heating portion of the ink preparation process.  
10 Specific examples of suitable antioxidants include (but are not limited to) (1) hydroquinone bis(2-hydroxyethyl) ether (Aldrich 23,791-4; hardness value 82), (2) 1H-benzotriazol-1-yl methyl isocyanide (Aldrich 36,799-0), (3) 2,6-di-tert-butyl-4-methoxy phenol (Aldrich 25,106-2), (4) 2,4-di-tert-butyl-6-(4-methoxybenzyl) phenol (Aldrich 23,008-1), (5) 4-bromo-2,6-  
15 dimethylphenol (Aldrich 34,951-8), (6) pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxy hydrocinnamate (hardness value 88; Aldrich 44,178-3), (7) 4-bromo-3,5-dimethylphenol (Aldrich B6,420-2), (8) 4-bromo-2-nitrophenol (Aldrich 30,987-7), (9) 4-(benzyloxy)phenol (Aldrich 27,293-0), and the like, as well as mixtures thereof. The antioxidants, when present, are present in  
20 any desired or effective amount, typically no less than about 0.25 percent by weight of the ink, and preferably no less than about 1 percent by weight of the ink, and typically no more than about 98 percent by weight of the ink, preferably no more than about 10 percent by weight of the ink, and more preferably no more than about 5 percent  
25 by weight of the ink, although the amount can be outside of these ranges.

The optional UV absorbers in the inks of the present invention primarily protect the images generated therewith from UV degradation. Specific examples of suitable UV absorbers include (but are not limited to) (1) 2-bromo-2',4-dimethoxyacetophenone (Aldrich 19,948-6), (2) 2-bromo-2',5'-dimethoxyacetophenone (Aldrich 10,458-2), (3) 2-bromo-3'-nitroacetophenone (Aldrich 34,421-4), (4) 2-bromo-4'-nitroacetophenone (Aldrich 24,561-5), (5) 3',5'-diacetoxyacetophenone (Aldrich 11,738-2), (6) 2-phenylsulfonyl acetophenone (Aldrich 34,150-3), (7) 3'-aminoacetophenone (Aldrich 13,935-1), (8) 4'-aminoacetophenone (Aldrich A3,800-2), (9) 1H-benzotriazole-1-acetonitrile (Aldrich 46,752-9), (10) 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (Aldrich 42,274-6), (11) 1,1-(1,2-ethane-diyl)bis(3,3,5,5-tetramethylpiperazinone) (commercially available from Goodrich Chemicals), (12) 2,2,4-trimethyl-1,2-hydroquinoline (commercially available from Mobay Chemical), (13) 2-(4-benzoyl-3-hydroxy phenoxy)ethylacrylate, (14) 2-dodecyl-N-(1,2,2,6,6-pentamethyl-4-piperidiny) succinimide (commercially available from Aldrich Chemical Co., Milwaukee, WI), (15) 2,2,6,6-tetramethyl-4-piperidiny/ $\beta,\beta,\beta',\beta'$ -tetramethyl-3,9-(2,4,8,10-tetraoxo spiro(5,5)-undecane) diethyl]-1,2,3,4-butane tetracarboxylate (commercially available from Fairmount), (16) N-p-ethoxycarbonylphenyl)-N'-ethyl-N'-phenylformadine (commercially available from Givaudan), (17) 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (commercially available from Monsanto Chemicals), (18) 2,4,6-tris-(N-1,4-dimethylpentyl-4-phenylenediamino)-1,3,5-triazine (commercially available from Uniroyal), (19) 2-dodecyl-N-(2,2,6,6-tetramethyl-4-piperidiny) succinimide (commercially available from Aldrich Chemical Co.), (20) N-(1-acetyl-2,2,6,6-tetramethyl-4-piperidiny)-2-dodecyl succinimide (commercially available from Aldrich Chemical

Co.), (21) [1,2,2,6,6-pentamethyl-4-piperidinyl/ $\beta,\beta\beta',\beta'$ -tetramethyl-3,9-(2,4,8,10-tetraoxo-spiro-(5,5)undecane)diethyl]-1,2,3,4-butane tetracarboxylate (commercially available from Fairmount), (22) [2,2,6,6-tetramethyl-4-piperidinyl]-1,2,3,4-butane tetracarboxylate (commercially available from Fairmount), (23) nickel dibutyl dithio carbamate (commercially available as UV-Chek AM-105 from Ferro), (24) 2-amino-2',5-dichlorobenzophenone (Aldrich 10,515-5), (25) 2'-amino-4',5'-dimethoxyacetophenone (Aldrich 32,922-3), (26) 2-benzyl-2-(dimethylamino)-4'-morpholino butyrophenone (Aldrich 40,564-7), (27) 4'-benzyloxy-2'-hydroxy-3'-methylacetophenone (Aldrich 29,884-0), (28) 4,4'-bis(diethylamino) benzophenone (Aldrich 16,032-6), (29) 5-chloro-2'-hydroxy benzophenone (Aldrich C4,470-2), (30) 4'-piperazinoacetophenone (Aldrich 13,646-8), (31) 4'-piperidinoacetophenone (Aldrich 11,972-5), (32) 2-amino-5-chlorobenzophenone (Aldrich A4,556-4), and the like, as well as mixtures thereof. When present, the UV absorber is present in the ink in any desired or effective amount, typically no less than about 0.25 percent by weight of the ink, and preferably no less than about 1 percent by weight of the ink, and typically no more than about 10 percent by weight of the ink, and preferably no more than about 5 percent by weight of the ink, although the amount can be outside of these ranges.

Other optional additives to the inks include biocides such as Dowicil 150, 200, and 75, benzoate salts, sorbate salts, and the like, present in an amount of from about 0.0001 to about 4 percent by weight of the ink, and preferably from about 0.01 to about 2.0 percent by weight of the ink, pH controlling agents such as acids or bases, phosphate salts, carboxylates salts, sulfite salts, amine salts, and the like,



The hardness of images can be measured with a Digital-Pencil style Durometer, Model 211B-00 PTC, obtained from Pacific Transducer Corporation, using ASTM Standard specifications for resistance to penetration with a conical [30 degrees included angle] indenter and  
 5 applying a 1 kilogram load. The hardness range for materials as measured with this instrument is from about 1 to about 100, the latter being the highest measurable value. It is believed that the images generated with the inks of the present invention, after cooling to ambient temperature (typically from about 20 to about 25°C, although  
 10 ambient temperature can be outside of this range) will exhibit hardness values of at least about 70 or more.

The inks of the present invention typically undergo, upon heating, a change from a solid state to a liquid state in a period of less than about 100 milliseconds, preferably less than about 50 milliseconds,  
 15 and more preferably less than about 10 milliseconds, although the time can be outside of these ranges. There is no necessary lower limit on this period of time for the inks; it is believed that practically achievable lower limits are around 5 milliseconds, although, if practically achievable, lower periods of time are acceptable.

The inks of the present invention typically exhibit acoustic-loss values of no more than about 100 decibels per millimeter, preferably no more than about 60 decibels per millimeter, and more preferably no more than about 40 decibels per millimeter, although the acoustic-loss value can be outside of these ranges. There is no  
 20 necessary lower limit on acoustic-loss value for the inks; it is believed that practically achievable lower limits are around 10 decibels per millimeter, although, if practically achievable, lower acoustic-loss  
 25



values of no more than about 25, preferably no more than about 10, and preferably no more than about 5, although the haze value can be outside of these ranges. There is no required lower limit on haze values. Haze values can be measured on images printed with the ink on  
5 uncoated polyester, such as MYLAR®, with a Haze meter XL-211, HAZEGARD® System obtained from Pacific Scientific Company.

The inks of the present invention generate images with desirable crease resistance. The images generated with the inks typically exhibit crease values of no more than about 0.6 millimeters,  
10 preferably no more than about 0.2 millimeters, and more preferably no more than about 0.1 millimeters, although the crease value can be outside of these ranges. There is no lower limit on crease values; ideally, this value is zero. The average width of the creased image can be measured by printing an image on paper, followed by (a) folding  
15 inwards the printed area of the image, (b) passing over the folded image a standard TEFLON® coated copper roll 2 inches in width, 3 inches in outer diameter, 2.25 inches in inner diameter, and weighing 860 grams, (c) unfolding the paper and wiping the loose ink from the creased imaged surface with a cotton swab, and (d) measuring the  
20 average width of the ink free creased area with an image analyzer. The crease value can also be reported in terms of area, especially when the image is sufficiently hard to break unevenly on creasing. Measured in terms of area, crease values of 60 millimeters correspond to about 0.6, crease values of 40 millimeters correspond to about 0.4,  
25 crease values of 10 millimeters correspond to about 0.1, and the like.

The ink compositions of the present invention can be prepared by any desired or suitable method. For example, the ink



ingredients can be mixed together, followed by heating, typically to a temperature of from about 100 to about 140°C, although the temperature can be outside of this range, and stirring until a homogeneous ink composition is obtained, followed by cooling the ink to ambient temperature (typically from about 20 to about 25°C). The inks of the present invention are solid at ambient temperature.

The present invention is also directed to a process which entails incorporating an ink of the present invention into an ink jet printing apparatus, melting the ink, and causing droplets of the melted ink to be ejected in an imagewise pattern onto a recording sheet. In one preferred embodiment, the printing apparatus employs an acoustic ink jet process, wherein droplets of the ink are caused to be ejected in imagewise pattern by acoustic beams. In a particularly preferred embodiment, the printing apparatus employs an acoustic ink jet printing process wherein droplets of the ink are formed by acoustic beams without imparting a substantial velocity component toward the print medium, using a droplet forming force that is sufficient only to form the ink droplets, and the printing process further comprises generating an electric field to exert an electrical force different from the droplet forming force on the ink droplets to move the ink droplets toward the print medium, and controlling the electrical force exerted on the formed complete ink droplets by the electric field.

Any suitable substrate or recording sheet can be employed, including plain papers such as Xerox® 4024 papers, Xerox® Image Series papers, Courtland 4024 DP paper, ruled notebook paper, bond paper, silica coated papers such as Sharp Company silica coated paper, JuJo paper, and the like, transparency materials,

5                   The inks of the present invention are particularly suitable for printing processes wherein the printing substrate, such as paper, transparency material, or the like, is heated during the printing process. When transparency substrates are employed, temperatures typically are no higher than from about 100 to about 110°C, since the polyester commonly employed as the base sheet in transparency sheets tends to deform at higher temperatures. Specially formulated transparencies and paper substrates can, however, tolerate higher temperatures, and frequently are suitable for exposure to temperatures of 150°C or even 200°C in some instances. Typical heating temperatures are from about 10 to about 140°C, and preferably from about 60 to about 95°C, although the temperature can be outside of these ranges.

Specific embodiments of the invention will now be described in detail. These examples are intended to be illustrative, and the invention is not limited to the materials, conditions, or process parameters set forth in these embodiments. All parts and percentages are by weight unless otherwise indicated.

Acoustic-loss measurements in the Examples were measured by placing samples of the materials between the two transducers with the temperature set at 150°C. The samples were allowed to equilibrate at 150°C for five minutes. The two transducers were then brought together to maximize the acoustic signal. The



Conductivity values in the Examples were measured under melt conditions at 150°C by placing an aluminum electrode in the melt and reading the resistivity output on a GenRad 1689 precision RLC Digibridge at a frequency of 1 kiloHertz. Conductivity was calculated  
5 from the resistivity data.

Crease values in the Examples were measured on solid area images printed on paper by (a) folding inwards the printed area of the image, (b) passing over the folded image a standard TEFLON® coated copper roll 2 inches in width, 3 inches in outer diameter, 2.25  
10 inches in inner diameter, and weighing 860 grams, (c) unfolding the paper and wiping the loose ink from the creased imaged surface with a cotton swab, and (d) measuring the average width of the ink free creased area with an image analyzer.

Haze values in the Examples were measured on images  
15 printed on uncoated polyester (such as MYLAR®) with a Haze meter XL-211, HAZEGARD® System, obtained from Pacific Scientific Company.

The spherulite sizes in the Examples were measured with an optical microscope with cross polarized light.

The hardness values in the Examples were measured with a  
20 Digital-Pencil style Durometer, Model 211B-00 PTC, obtained from Pacific Transducer Corporation, using ASTM Standard specifications for resistance to penetration with a conical [30 degrees included angle] indenter and applying a 1 kilogram load. The hardness range for materials as measured with this instrument is from about 1 to about 100,  
25 the latter being the highest measurable value.

The gloss values in the Examples were obtained on a 75° Glossmeter, Glossgard II, obtained from Pacific Scientific (Gardner/Neotec Instrument Division).

5

### **EXAMPLE I**

A black phase-change ink was prepared by mixing 10 percent by weight poly ( $\alpha$ -methyl styrene) (hardening component;  $M_n$ =790; Aldrich 19,183-3; hardness value 92), 30 percent by weight 4-hexyl resorcinol (ink vehicle; Aldrich 20,946-5; acoustic-loss value 28  
10 decibels per millimeter; melting point 67°C), 30 percent by weight 2-(1-adamantyl)-4-methyl phenol (viscosity modifier; Aldrich 39,468-8; acoustic-loss value 34 decibels per millimeter; melting point 130°C), 20 percent by weight 1-(*p*-toluene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 24,424-4; melting point 79°C; acoustic-loss  
15 value 35 decibels per millimeter; conductivity 8.0 log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Neozapon Black X51 dye (C.I. Solvent Black; C.I. 12195; obtained from BASF). This mixture was then diluted with methyl ethyl  
20 ketone (for 10 grams of the solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink  
25 became free of the solvent, which was recycled. Subsequently the mixture was cooled to 25°C. This black ink exhibited an acoustic-loss value of 60 decibels per millimeter, a viscosity of 8.5 centipoise at

150°C, and a conductivity of 6.6 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

5

## **EXAMPLE II**

A blue phase-change ink was prepared by mixing 10 percent by weight poly(vinyl toluene-co- $\alpha$ -methyl styrene) (hardening component; Aldrich 45,722-1; hardness value 90), 30 percent by weight 4-dodecyl resorcinol (ink vehicle; Aldrich D22,260-7), 30 percent by weight 4,4'-dimethyl biphenyl (viscosity modifier; Aldrich D15,120-3; acoustic-loss value 28 decibels per millimeter; melting point 119°C), 20 percent by weight 1-(p-toluene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 24,417-1; melting point 133°C; acoustic-loss value 39 decibels per millimeter; conductivity 8.4 log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Sudan Blue 670 dye (C.I. 61554; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which was recycled. Subsequently the mixture was cooled to 25°C. This blue ink exhibited an acoustic-loss value of 62 decibels per millimeter, a viscosity of 8.7 centipoise at 150°C, and a conductivity of 6.6 log(picomho/cm) at 150°C, and when

applied to paper generated images with a hardness value of 81 at 23°C.

### **EXAMPLE III**

5                   A yellow phase-change ink was prepared by mixing 10 percent by weight poly (styrene-co-allyl alcohol) (hardening component;  $M_n=1200$ ; 60 mole percent styrene; Aldrich 46,813-4; hardness value 91.6), 30 percent by weight 4-(tert-octyl)phenol (ink vehicle; melting point 84°C; Aldrich 29,082-3; acoustic-loss value 36  
10   decibels per millimeter), 30 percent by weight triphenyl methane (viscosity modifier; Aldrich 10,130-3; hardness value 76.4; acoustic-loss value 24 decibels per millimeter; melting point 94°C), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 40,948-0; melting point 126°C; acoustic-loss  
15   value 39 decibels per millimeter; conductivity 8.0 log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Sudan Yellow 146 dye (C.I. 12700; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the  
20   solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which  
25   was recycled. Subsequently the mixture was cooled to 25°C. This yellow ink exhibited an acoustic-loss value of 67 decibels per millimeter, a viscosity of 8.3 centipoise at 150°C, and a conductivity of 6.8

log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

#### **EXAMPLE IV**

- 5                   A magenta phase-change ink was prepared by mixing 10 percent by weight poly ( $\alpha$ -methyl styrene) (hardening component;  $M_n$ =790; Aldrich 19,183-3; hardness value 92), 30 percent by weight 4-bromo-N-dodecyl-1-hydroxy-2-naphthalene carboxamide (ink vehicle; Aldrich 37,157-2; acoustic-loss value 42 decibels per millimeter; melting
- 10 point 96°C), 30 percent by weight diphenylfulvene, (viscosity modifier; Aldrich D20,770-5; acoustic-loss value 32 decibels per millimeter; melting point 82°C), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 40,948-0; melting point 128°C; acoustic-loss value 38 decibels per millimeter;
- 15 conductivity 8.1 log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Sudan Red 462 dye (C.I. 26050; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the solid ink mixture the amount of
- 20 solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which was recycled.
- 25 Subsequently the mixture was cooled to 25°C. This red ink exhibited an acoustic-loss value of 65 decibels per millimeter, a viscosity of 8.9 centipoise at 150°C, and a conductivity of 6.8 log(picomho/cm) at



150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

#### **EXAMPLE V**

5                Each of the inks prepared as described in Examples I through IV was incorporated into an acoustic ink jet printing test fixture utilizing the ejection mechanism disclosed in *J. Appl. Phys.*, 65(9), 1 May 1989, and references therein, the disclosures of each of which are totally incorporated herein by reference. A jetting frequency of 160  
10 MHz was used to generate drops of about 2 picoliters, up to 12 drops per pixel at 600 spi. The images formed on paper exhibited excellent color quality, optical density values of 2.65 (black), 1.95 (cyan), 2.25 (magenta), and 1.50 (yellow), sharp edges, and waterfastness and lightfastness values of greater than 95%. The images obtained with  
15 these conductive inks on paper were folded and creased. The crease values (measured in terms of area and subsequently converted to millimeters) were 0.12 (black), 0.08 (cyan), 0.09 (magenta), and 0.07 (yellow). The gloss values for the images were 85 (black), 82 (magenta), 81 (cyan), and 85 (yellow). The ink spherulite radius was  
20 measured at 1 to 2.5 microns, leading to haze values of 7 to 12 when printed on transparency substrates.

#### **EXAMPLE VI**

25                A black phase-change ink was prepared by mixing 10 percent by weight poly ( $\alpha$ -methyl styrene) (hardening component;  $M_n=790$ ; Aldrich 19,183-3; hardness value 92), 30 percent by weight 4-hexyl resorcinol (ink vehicle; Aldrich 20,946-5; acoustic-loss value 28

decibels per millimeter; melting point 67°C), 30 percent by weight 1,2,3,6,7,8-hexa hydropyrene (viscosity modifier; Aldrich H960-5; acoustic-loss value 39 decibels per millimeter; melting point 133°C), 20 percent by weight 1-(p-toluene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 24,424-4; melting point 79°C; acoustic-loss value 35 decibels per millimeter; conductivity 8.0 log(picomho/cm)), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Neozapon Black X51 dye (C.I. Solvent Black; C.I. 12195; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which was recycled. Subsequently the mixture was cooled to 25°C. This black ink exhibited an acoustic-loss value of 62 decibels per millimeter, a viscosity of 8.3 centipoise at 150°C, and a conductivity of 6.7 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 81 at 23°C.

### **EXAMPLE VII**

A blue phase-change ink was prepared by mixing 10 percent by weight poly(vinyl toluene-co- $\alpha$ -methyl styrene) (hardening component; Aldrich 45,722-1; hardness value 90), 30 percent by weight 4-dodecyl resorcinol (ink vehicle; Aldrich D22,260-7), 30 percent by weight 1,2,3,6,7,8-hexa hydropyrene (viscosity modifier; Aldrich H960-5;

acoustic-loss value 39 decibels per millimeter; melting point 133°C), 20 percent by weight 1-(p-toluene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 24,417-1; melting point 133°C; acoustic-loss value 39 decibels per millimeter; conductivity 8.4 log(picomho/cm)), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Sudan Blue 670 dye (C.I. 61554; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which was recycled. Subsequently the mixture was cooled to 25°C. This blue ink exhibited an acoustic-loss value of 64 decibels per millimeter, a viscosity of 8.5 centipoise at 150°C, and a conductivity of 6.7 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 83 at 23°C.

20

### **EXAMPLE VIII**

A yellow phase-change ink was prepared by mixing 10 percent by weight poly (styrene-co-allyl alcohol) (hardening component;  $M_n=1200$ ; 60 mole percent styrene; Aldrich 46,813-4; hardness value 91.6), 30 percent by weight 4-(tert-octyl) phenol (ink vehicle; melting point 84°C; Aldrich 29,082-3; acoustic-loss value 36 decibels per millimeter; melting point 84°C), 30 percent by weight 9-fluorenone (viscosity modifier; Aldrich F,150-6; hardness value 68.6;

acoustic-loss value 28 decibels per millimeter; melting point 85°C), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl) imidazole (Aldrich 40,948-0; melting point 126°C; acoustic-loss value 39 decibels per millimeter; conductivity 8.0 log(picomho/cm)), 5 percent by weight  
 5 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Sudan Yellow 146 dye (C.I. 12700; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of  
 10 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which was recycled. Subsequently the mixture was cooled to 25°C. This yellow ink exhibited an acoustic-loss  
 15 value of 67 decibels per millimeter, a viscosity of 8.3 centipoise at 150°C, and a conductivity of 6.9 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

20

### **EXAMPLE IX**

A magenta phase-change ink was prepared by mixing 10 percent by weight poly ( $\alpha$ -methyl styrene) (hardening component;  $M_n$ =790; Aldrich 19,183-3; hardness value 92), 30 percent by weight 4-bromo-N-dodecyl-1-hydroxy-2-naphthalene carboxamide (ink vehicle;  
 25 Aldrich 37,157-2; acoustic-loss value 42 decibels per millimeter; melting point 96°C), 30 percent by weight phenanthrene (viscosity modifier; Aldrich P1,140-9; hardness value 73.8; acoustic-loss value 35 decibels

per millimeter; melting point 101°C), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 40,948-0; melting point 128°C; acoustic-loss value 38 decibels per millimeter; conductivity 8.1 log(picomho/cm)), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Sudan Red 462 dye (C.I. 26050; obtained from BASF). This mixture was then diluted with methyl ethyl ketone (for 10 grams of the solid ink mixture the amount of solvent was 15 grams). The resulting slurry was then heated to a temperature of 100°C with constant stirring to impart color to the ink. After 30 minutes, the temperature was raised to 140°C and stirred for a period of 60 minutes until a homogeneous solution formed. During this period, the ink became free of the solvent, which was recycled. Subsequently the mixture was cooled to 25°C. This red ink exhibited an acoustic-loss value of 61 decibels per millimeter, a viscosity of 8.4 centipoise at 150°C, and a conductivity of 6.7 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

20

#### **EXAMPLE X**

Each of the inks prepared as described in Examples VI through IX was incorporated into an acoustic ink jet printing test fixture and tested as described in Example V. The images formed on paper exhibited excellent color quality, optical density values of 2.68 (black), 1.99 (cyan), 2.27 (magenta), and 1.55 (yellow), sharp edges, and lightfastness and waterfastness values of greater than 95%. The images obtained with these conductive inks on paper were folded and

creased. The crease values (measured in terms of area and subsequently converted to millimeters) were 0.11 (black), 0.10 (cyan), 0.07 (magenta), and 0.08 (yellow). The gloss values for the images were 82 (black), 81 (magenta), 81 (cyan), and 87 (yellow). The ink spherulite radius was measured at 1 to 2.5 microns, leading to haze values of 7 to 12 when printed on transparency substrates.

### **EXAMPLE XI**

A black phase-change ink was prepared by mixing 10 percent by weight poly ( $\alpha$ -methyl styrene) (hardening component;  $M_n=790$ ; Aldrich 19,183-3; hardness value 92), 30 percent by weight 1-pyrenemethanol (viscosity modifier; Aldrich 38,943-9; melting point 126°C; acoustic loss value 45 decibels per millimeter), 30 percent by weight 4-hydroxy-3-methoxy benzaldehyde (solid dye solvent; Aldrich V,110-4; hardness value 74.5; acoustic-loss value 30 decibels per millimeter; melting point 83°C), 20 percent by weight 1-(p-toluene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 24,424-4; melting point 79°C; acoustic-loss value 35 decibels per millimeter; conductivity 8.0 log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Neozapon Black X51 dye (C.I. Solvent Black; C.I. 12195; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This black ink exhibited an acoustic-loss value of 69 decibels per millimeter, a viscosity of 8.3 centipoise at 150°C, and a

conductivity of 6.7 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 81 at 23°C.

### **EXAMPLE XII**

5                   A blue phase-change ink was prepared by mixing 10 percent by weight poly(vinyl toluene-co- $\alpha$ -methyl styrene) (hardening component; Aldrich 45,722-1; hardness value 90), 30 percent by weight phenanthrene (viscosity modifier; Aldrich P1,140-9; hardness value 73.8; melting point 100°C; acoustic loss value 40 decibels per millimeter), 30  
10 percent by weight 4-acetoxy-3,5-dimethoxy benzaldehyde (solid dye solvent; Aldrich 38,774-6; hardness value 79.5; acoustic-loss value 30 decibels per millimeter; melting point 119°C), 20 percent by weight 1-(p-toluene sulfonyl)-3-nitro-1,2,4-triazole, (conductivity enhancing agent; Aldrich 24,417-1; melting point 117°C; acoustic-loss value 39 decibels  
15 per millimeter; conductivity 8.4 (log(picomho/cm))), 5 percent by weight hydroquinone bis(2-hydroxyethyl)ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Sudan Blue 670 dye (C.I. 61554; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes  
20 until it formed a homogeneous solution, and subsequently cooled to 25°C. This blue ink exhibited an acoustic-loss value of 68 decibels per millimeter, a viscosity of 8.6 centipoise at 150°C, and a conductivity of 6.6 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 81 at 23°C.

25

### **EXAMPLE XIII**

A yellow phase-change ink was prepared by mixing 10 percent by weight poly(methyl styrene-co-indene) hydrogenated (hardening agent;  $M_n=750$ ;  $T_g=72^\circ\text{C}$ ; Aldrich 45,722-1; hardness value 92), 30 percent by weight 1,3-diphenyl isobenzofuran (viscosity modifier; Aldrich 10,548-1; hardness value 62; acoustic-loss value 32 decibels per millimeter; melting point  $130^\circ\text{C}$ ), 30 percent by weight 2,6-dimethoxybenzaldehyde (solid dye solvent; Aldrich 29,250-8; acoustic-loss value 22 decibels per millimeter; melting point  $98^\circ\text{C}$ ), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 40,948-0; melting point  $126^\circ\text{C}$ ; acoustic loss value 39 decibels per millimeter; conductivity 8.0 (log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point  $101^\circ\text{C}$ ; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Sudan Yellow 146 dye (C.I. 12700; obtained from BASF). The mixture was heated to a temperature of about  $140^\circ\text{C}$ , stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to  $25^\circ\text{C}$ . This yellow ink exhibited an acoustic-loss value of 71 decibels per millimeter, a viscosity of 8.4 centipoise at  $150^\circ\text{C}$ , and a conductivity of 6.9 log(picomho/cm) at  $150^\circ\text{C}$ , and when applied to paper generated images with a hardness value of 79 at  $23^\circ\text{C}$ .

### **EXAMPLE XIV**

A magenta phase-change ink was prepared by mixing 10 percent by weight polylimonene (hardening component; Aldrich 45,755-8; hardness value 84.8), 30 percent by weight 1-acetylpyrene



(viscosity modifier; Aldrich 39,142-8; acoustic-loss value 42 decibels per millimeter; melting point 89°C), 30 percent by weight terephthal dicarboxaldehyde (solid dye solvent; Aldrich T220-7; hardness value 73; acoustic-loss value 33 decibels per millimeter; melting point 116°C), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 40,948-0; melting point 128°C; acoustic-loss value 38 decibels per millimeter; conductivity 8.1 (log(picomho/cm))), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight Sudan Red 462 dye (C.I. 26050; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This magenta ink exhibited an acoustic-loss value of 67 decibels per millimeter, a viscosity of 8.7 centipoise at 150°C, and a conductivity of 6.9 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 81 at 23°C.

#### **EXAMPLE XV**

Each of the inks prepared as described in Examples XI through XIV was incorporated into an acoustic ink jet printing test fixture utilizing the ejection mechanism disclosed in *J. Appl. Phys.*, 65(9), 1 May 1989, and references therein, the disclosures of each of which are totally incorporated herein by reference. A jetting frequency of 160 MHz was used to generate drops of about 2 picoliters, up to 12 drops per pixel at 600 spi. The images formed on paper exhibited excellent color quality, optical density values of 2.85 (black), 1.98 (cyan), 2.35

(magenta), and 1.55 (yellow), sharp edges, and waterfastness and lightfastness values of greater than 95%. The images obtained with these conductive inks on paper were folded and creased. The crease values (measured in terms of area and subsequently converted to millimeters) were 0.11 (black), 0.08 (cyan), 0.08 (magenta), and 0.08 (yellow). The gloss values for the images were 87 (black), 81 (magenta), 82 (cyan), and 85 (yellow). The ink spherulite radius was measured at 1 to 3 microns, leading to haze values of 12 to 18 when printed on transparency substrates.

10

### **EXAMPLE XVI**

A black phase-change ink was prepared by mixing 10 percent by weight poly ( $\alpha$ -methyl styrene) (hardening component;  $M_n=790$ ; Aldrich 19,183-3; hardness value 92), 30 percent by weight dibenzosuberol (viscosity modifier; Aldrich D10,497-3; acoustic-loss value 26 decibels per millimeter; melting point 92 °C), 30 percent by weight 4-acetoxy-3-methoxy cinnamaldehyde (solid dye solvent; Aldrich 42,754-3; acoustic-loss value 33 decibels per millimeter; melting point 100°C), 20 percent by weight 1-(p-toluene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 24,424-4; melting point 79°C; acoustic-loss value 35 decibels per millimeter; conductivity 8.0 (log(picomho/cm))), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Neozapon Black X51 dye (C.I. Solvent Black; C.I. 12195; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This black ink exhibited an acoustic-

loss value of 65 decibels per millimeter, a viscosity of 8.3 centipoise at 150°C, and a conductivity of 6.8 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

5

### **EXAMPLE XVII**

A blue phase-change ink was prepared by mixing 5 percent by weight poly(vinyl toluene-co- $\alpha$ -methyl styrene) (hardening component; Aldrich 45,722-1; hardness value 90), 30 percent by weight dibenzosuberol (viscosity modifier; Aldrich D10,497-3; acoustic-loss value 31 decibels per millimeter; melting point 92°C), 30 percent by weight 4-acetoxy-3-methoxy cinnamaldehyde (solid dye solvent; melting point 100°C; Aldrich 42,754-3), 5 percent by weight poly (p-toluene sulfonamide-co-formaldehyde) (solid dye solvent; Aldrich 28,076-3; hardness value 90), 20 percent by weight 1-(p-toluene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 24,417-1; melting point 133°C; acoustic-loss value 39 decibels per millimeter; conductivity 8.4 (log(picomho/cm))), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Sudan Blue 670 dye (C.I. 61554; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This blue ink exhibited an acoustic-loss value of 68 decibels per millimeter, a viscosity of 8.5 centipoise at 150°C, and a conductivity of 6.6 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 81 at 23°C.

### **EXAMPLE XVIII**

A yellow phase-change ink was prepared by mixing 5 percent by weight poly (methyl styrene-co-indene) hydrogenated (hardening component;  $M_n=750$ ;  $T_g=72^\circ\text{C}$ ; Aldrich 45,722-1; hardness value 92), 30 percent by weight 9-acetylphenanthrene (viscosity modifier; Aldrich A1,960-1; acoustic-loss value 38 decibels per millimeter; melting point  $74^\circ\text{C}$ ), 30 percent by weight terephthal dicarboxaldehyde (solid dye solvent; Aldrich T220-7; hardness value 73), 5 percent by weight poly ((phenyl glycidyl ether)-co-formaldehyde) (solid dye solvent;  $M_n=570$ ; Aldrich 40,676-7), 20 percent by weight 1-(2,4,6-triisopropyl benzene sulfonyl) imidazole (conductivity enhancing agent; Aldrich 40,948-0; melting point  $126^\circ\text{C}$ ; acoustic-loss value 39 decibels per millimeter; conductivity 8.0 (log(picomho/cm))), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point  $105^\circ\text{C}$ ; Aldrich 25,106-2), and 5 percent by weight Sudan Yellow 146 dye (C.I. 12700; obtained from BASF). The mixture was heated to a temperature of about  $140^\circ\text{C}$ , stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to  $25^\circ\text{C}$ . This yellow ink exhibited an acoustic-loss value of 72 decibels per millimeter, a viscosity of 8.7 centipoise at  $150^\circ\text{C}$ , and a conductivity of 6.8 log(picomho/cm) at  $150^\circ\text{C}$ , and when applied to paper generated images with a hardness value of 81 at  $23^\circ\text{C}$ .

### **EXAMPLE XIX**

A magenta phase-change ink was prepared by mixing 5 percent by weight polylimonene (hardening component; Aldrich

45,755-8; hardness value 84.8), 30 percent by weight 9-acetylphenanthrene (viscosity modifier; Aldrich A1,960-1; acoustic-loss value 40 decibels per millimeter; melting point 74°C), 30 percent by weight 2,6-dimethoxybenzaldehyde (solid dye solvent; melting point 98°C; Aldrich 29,250-8), 5 percent by weight poly ((phenyl glycidyl ether)-co-formaldehyde) (solid dye solvent;  $M_n=570$ ; Aldrich 40,676-7), 20 percent by weight 1-(2,4,6-trisopropyl benzene sulfonyl)-3-nitro-1,2,4-triazole (conductivity enhancing agent; Aldrich 40,948-0; melting point 128°C; acoustic-loss value 38 decibels per millimeter; conductivity 8.1 (log(picomho/cm))), 5 percent by weight 2,6-di-tert-butyl-4-methoxyphenol (antioxidant; melting point 105°C; Aldrich 25,106-2), and 5 percent by weight Sudan Red 462 dye (C.I. 26050; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This red ink exhibited an acoustic-loss value of 71 decibels per millimeter, a viscosity of 8.7 centipoise at 150°C, and a conductivity of 6.7 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 80 at 23°C.

20

### **EXAMPLE XX**

Each of the inks prepared as described in Examples XVI through XIX was incorporated into an acoustic ink jet printing test fixture and tested as described in Example XV. The images formed on paper exhibited excellent color quality, optical density values of 2.78 (black), 1.97 (cyan), 2.23 (magenta), and 1.50 (yellow), sharp edges, and lightfastness and waterfastness values of greater than 95%. The

images obtained with these conductive inks on paper were folded and creased. The crease values (measured in terms of area and subsequently converted to millimeters) were 0.11 (black), 0.09 (cyan), 0.08 (magenta), and 0.08 (yellow). The gloss values for the images were 80 (black), 81 (magenta), 81 (cyan), and 83 (yellow). The ink spherulite radius was measured at 1 to 3 microns, leading to haze values of 12 to 18 when printed on transparency substrates.

### **EXAMPLE XXI**

10           A black phase-change ink was prepared by mixing 15 percent by weight polylimonene (hardening component; Aldrich 45,755-8; hardness value 84.8), 30 percent by weight 1-adamantyl bromomethyl ketone (viscosity modifier; Aldrich 14,929-2; acoustic-loss value 25 decibels per millimeter; melting point 79°C), 45 percent by weight methyl 1-adamantane sulfonate (conductivity enhancing agent; Aldrich 40,956-1; melting point 115°C; acoustic-loss value 35 decibels per millimeter; conductivity 9.0 log(picomho/cm)), 5 percent by weight hydroquinone bis(2-hydroxyethyl) ether (antioxidant; melting point 101°C; Aldrich 23,791-4; hardness value 82), and 5 percent by weight  
20   Neozapon Black X51 dye (C.I. Solvent Black; C.I. 12195; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This black ink exhibited an acoustic-loss value of 55 decibels per millimeter, a viscosity of 10.8 centipoise at  
25   150°C, and a conductivity of 7.5 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 82.5 at 23°C.

### **EXAMPLE XXII**

A blue phase-change ink was prepared by mixing 15 percent by weight poly- $\beta$ -pinene (hardening component; Aldrich 45,752-3; hardness value 85.8), 30 percent by weight dibenzosuberone (viscosity modifier; Aldrich D3,173-7; hardness value 85.2), 45 percent by weight octadecyl-4-chlorobenzene sulfonate (Aldrich 47,799-0; melting point 66°C; acoustic-loss value 32 decibels per millimeter; conductivity 8.8 log(picomho/cm), 5 percent by weight 1H-benzotriazol-1-yl methyl isocyanide (antioxidant; Aldrich 36,799-0), and 5 percent by weight Sudan Blue 670 dye (C.I. 61554; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This blue ink exhibited an acoustic-loss value of 52 decibels per millimeter, a viscosity of 10.7 centipoise at 150°C, and a conductivity of 7.4 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 82 at 23°C.

### **EXAMPLE XXIII**

A yellow phase-change ink was prepared by mixing 10 percent by weight polylimonene (hardening component; Aldrich 45,755-8; hardness value 84.8), 35 percent by weight bis(phenylsulfonyl) methane (viscosity modifier; Aldrich 30,296-1; acoustic-loss value 29 decibels per millimeter; melting point 122°C), 45 percent by weight tetrabutylammonium trifluoromethanesulfonate (conductivity enhancing agent; Aldrich 34,509-1; melting point 72°C; acoustic-loss value 29

decibels per millimeter; conductivity 8.8 log(picomho/cm), 5 percent by weight 4-bromo-2,6-dimethyl phenol (antioxidant; Aldrich 34,951-8), and 5 percent by weight Sudan Yellow 146 dye (C.I. 12700; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This yellow ink exhibited an acoustic-loss value of 56 decibels per millimeter, a viscosity of 10.7 centipoise at 150°C, and a conductivity of 7.8 log(picomho/cm) at 150°C, and when applied to paper generated images with a hardness value of 82.5 at 23°C.

#### **EXAMPLE XXIV**

A magenta phase-change ink was prepared by mixing 10 percent by weight poly-β-pinene (hardening component; Aldrich 45,752-3; hardness value 85.8), 35 percent by weight 1,6-bis(diphenyl phosphino) hexane (viscosity modifier; Aldrich 28,798-9; acoustic-loss value 36 decibels per millimeter; melting point 125°C), 45 percent by weight S,S'-ethylene-p-toluene thiosulfonate (conductivity enhancing agent; Aldrich 23,257-2; melting point 75°C; acoustic-loss value 37 decibels per millimeter; conductivity 8.8 log(picomho/cm), 5 percent by weight 4-(benzyloxy)phenol (antioxidant; Aldrich 27,293-0), and 5 percent by weight Sudan Red 462 dye (C.I. 26050; obtained from BASF). The mixture was heated to a temperature of about 140°C, stirred for a period of about 60 minutes until it formed a homogeneous solution, and subsequently cooled to 25°C. This red ink exhibited an acoustic-loss value of 57 decibels per millimeter, a viscosity of 10.5 centipoise at 150°C, and a conductivity of 7.9 log(picomho/cm) at 150°C, and when



applied to paper generated images with a hardness value of 81 at 23°C.

#### **EXAMPLE XXV**

5                Each of the inks prepared as described in Examples XXI through XXIV was incorporated into an acoustic ink jet printing test fixture utilizing the ejection mechanism disclosed in *J. Appl. Phys.*, 65(9), 1 May 1989, and references therein, the disclosures of each of which are totally incorporated herein by reference. A jetting frequency of 160  
10 MHz was used to generate drops of about 2 picoliters, up to 12 drops per pixel at 600 spi. The images formed on paper exhibited excellent color quality, optical density values of 2.55 (black), 1.95 (cyan), 2.55 (magenta), and 1.75 (yellow). The images obtained with these conductive inks on paper were folded and creased. The crease values  
15 (measured in terms of area and subsequently converted to millimeters) were 0.08 (black), 0.06 (cyan), 0.05 (magenta), and 0.05 (yellow). The gloss values for the images were 80 (black), 81 (magenta), 83 (cyan), and 80 (yellow). The ink spherulite radius was measured at 1 to 2.5 microns, leading to haze values of 10 to 15 when printed on  
20 transparency substrates.

Other embodiments and modifications of the present invention may occur to those of ordinary skill in the art subsequent to a review of the information presented herein; these embodiments and  
25 modifications, as well as equivalents thereof, are also included within the scope of this invention.